



PATENT SPECIFICATION

607,735

Convention Date (United States of America): Feb. 9, 1945.

Application Date (In United Kingdom): Feb. 11, 1946.

No. 4173/46

Complete Specification Accepted: Sept. 3, 1948.

Index at acceptance:—Class 2(iii), R4c(12: 16), R4d(1: 3: 4: 5: 6: 7).

COMPLETE SPECIFICATION

Polymerization of Monoethylenic Compounds

We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organised and existing under the laws of the State of Delaware, of Wilmington, Delaware, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the polymerization of monoethylenic compounds. According to the present invention in the process of polymerizing one or more polymerizable monoethylenic compounds having the group $\text{CH}_2=\text{C}<$ in the presence of an oxygen-liberating polymerization catalyst, and in the presence of water and/or other associated hydroxylated liquid having a molecular weight up to 61, we provide the improvement which comprises promoting the effect of said catalyst by the presence of a compound of a heavy metal capable of existing in more than one state of valence, said compound being present in a reduced state.

We have discovered that the polymerizing activity of the oxygen-liberating catalysts, such as hydrogen peroxide, is greatly promoted by the presence of suitable amounts of a reduced heavy metal compound, for example ferrous sulphate, and that such heavy metal compounds, in the reduced state, are much more effective as catalyst promoters than when in the oxidized state.

If a reduced heavy metal compound, such as ferrous sulphate, is added, for example to an aqueous emulsion of a polymerizable mono-olefinic compound such as a vinyl ester containing a peroxide as polymerization catalyst, the iron compound will be effective as a catalyst promoter so long as it remains in the reduced state. However, it is rapidly oxidized by the peroxide and both the ferrous salt and the peroxide must be replenished to maintain a high rate of polymerization. Such

method of practising the invention is in most cases undesirable, chiefly because of the resultant contamination of the polymer with a relatively large amount of the metal salt and the relatively high consumption of the peroxide. Therefore, we prefer to add also a reducing agent which will maintain at least an effective proportion of the heavy metal compound in the reduced state.

A useful criterion for choosing an efficient reducing agent is that under the conditions prevailing while polymerization proceeds, the reducing agent must be capable of reducing ferric iron compounds to ferrous iron compounds in the presence of the oxygen-liberating compound selected as polymerization catalyst. We have found, also, that the hydrogen ion concentration affects the results in that the operability of the various reducing agents varies with the pH. Some reducing agents are operative only under acidic conditions, and others only under alkaline conditions. Some are effective over a wide range of pH, while others are effective only in a limited pH range.

The following examples illustrate but do not limit the invention:—

EXAMPLE I.

50 ml. of vinyl acetate is added to 500 ml. of water in a three-neck round bottom flask. The mixture is agitated slowly. 25 ml. of 0.0242 M hydrogen peroxide and 50 ml. of 0.035 M zinc formaldehyde sulphonylate is added. Then 5 drops of a 1 per cent ferrous ammonium sulphate solution is added. The temperature at the start of the polymerization is 24.4° C. After 18 minutes, the temperature is 39.8° C.; analysis showed that 95.8 per cent of the vinyl acetate is polymerized. The pH of the system is about 3.5. With hydrogen peroxide alone, no polymer forms under these conditions.

EXAMPLE II.

To 20 ml. of styrene there is added 2 g. of soap flakes, which contain 10 to 20 parts

[Price 3/-]

Price 3s. 6d.

Price 4s. 6d.

per million of iron compounds, in a three-neck round bottom flask equipped with a stirrer. 100 ml. of water is added slowly with agitation giving a dispersion of 5 styrene in soapy water. 6.4 ml. of 0.4 N caustic soda is added. Then 4 ml. of 1.1 M hydrogen peroxide and 0.2 ml. of butyraldehyde are added. The initial temperature of the mixture is 27.7° C. After 10 10 minutes the temperature of the mixture is 44.4° C. An analysis showed that 93 per cent of the styrene is polymerized. The initial pH of the mixture is 11.6 and the

final pH 10.83. Hydrogen peroxide alone will not polymerize styrene under these 15 conditions.

The following Table shows a group of activated systems, generally comparable to those of the foregoing examples, together with the monomers which have 20 been rapidly and efficiently polymerized with these systems in accordance with the process of the present invention. In the Table, the reducing agents are grouped according to the pH ranges in which they 25 are effective:—

TABLE

Reducing Agents Effective in the pH range : 1 to 5

Activated System

Compound Polymerized	Catalyst	Reducing Agent	Metal Compound Promoters
Vinyl acetate	Hydrogen peroxide	Sodium formaldehyde sulfoxylate ($\text{NaHSO}_2 \cdot \text{CH}_2\text{O}$) or Zinc sulfoxylate ($\text{Zn}(\text{HSO}_2 \cdot \text{CH}_2\text{O})_2$)	Iron or Vanadium
Vinyl cyanide	"	"	"
Methyl methacrylate	"	"	"
Vinylidene Chloride	"	"	"
Vinyl acetate	"	1-Ascorbic acid or d-Ascorbic acid	Iron
Vinyl cyanide	"	"	"
Methyl methacrylate	"	"	"
Vinyl acetate	"	Oxidized glucose or Reductone	"
Vinyl acetate	"	Dihydroxy maleic acid	"
Styrene	"	Sodium formaldehyde sulfoxylate	"
Styrene	"	Ascorbic Acid	"
Vinyl acetate	Ammonium persulphate	Ascorbic Acid	Iron
Vinyl acetate	Tert.-butyl hydroperoxide	Sodium formaldehyde sulfoxylate	"
Vinyl acetate	Peracetic acid	Ascorbic acid	"
Copolymers			
Vinyl acetate with Vinyl cyanide	Hydrogen peroxide	Sodium formaldehyde sulfoxylate	"
Vinyl acetate with Methylmethacrylate	"	"	"
Vinyl cyanide with Vinylidene chloride	"	"	"
Vinyl acetate, Vinyl cyanide and Vinylidene chloride	"	Sodium formaldehyde sulfoxylate and Ascorbic acid	"

Reducing Agents Effective in the pH Range : 7 to 9.

Compound Polymerized	Catalyst	Reducing Agent	Metal Compound Promoters
Methyl methacrylate	Hydrogen peroxide	Sodium sulphite	Iron, Copper, Cobalt or Nickel.
Methyl methacrylate	"	Thiourea peroxide or Formamidine sulphinic acid.	Iron
Methyl methacrylate	"	d-Isoascorbic acid	Copper, Iron or Vanadium.
Vinyl acetate	"	Formamidine sulphinic acid	Iron
Methyl methacrylate	"	Oxidized glucose	"

Reducing Agents Effective in the pH Range : 10 to 13.

Compound Polymerized	Catalyst	Reducing Agent	Metal Compound Promoters
Styrene	Hydrogen peroxide	Butyraldehyde, Acetaldehyde, Propionaldehyde, Cinnamic aldehyde, Citronellal Iso-butyraldehyde, Heptaldehyde or Benzaldehyde.	Iron
Styrene	Hydrogen peroxide	Acetone, Methyl amyl ketone, Di-isopropyl ketone, Di-acetone alcohol, Phorone or Acetyl-acetone.	"
Styrene	Hydrogen peroxide	Pyrogallol	"
"	"	Pinene	"
"	"	Propylene Oxide	"
"	"	d-Levulose	"
"	"	1-Ascorbic Acid	"
"	Sodium peroxide	n-Butyraldehyde	"
"	Sodium percarbonate	"	"
"	Sodium perborate	"	"
"	Hydrogen peroxide	Methyl acetoacetate	"
"	"	Ethyl acetone dicarboxylate	"
"	Ammonium persulphate	Methyl acetoacetate	"

By reference to the above Table it may be seen that the selection of a suitable system will usually depend upon the conditions under which the system is to be operated. Thus, it has been found that the same reducing agent will not necessarily function effectively over the entire pH range from 1 to 14. In order to determine whether the reducing agent is a satisfactory one to employ, under the conditions of operation, it has been found desirable to make qualitative tests to determine whether such reducing agent will rapidly reduce ferric ions to ferrous ions under the prevailing conditions. It is also desirable to determine whether the reducing agent will rapidly destroy the

peroxygen compound under the same conditions. As an example of how these tests can be satisfactory made, tests will be described as performed on a system which is to contain sodium formaldehyde sulfoxylate (a reducing agent commercially employed for reducing dyestuffs), ferric ammonium sulphate and hydrogen peroxide. If, to water, one adds a few drops of a dilute ferric ammonium sulphate solution and a small amount of potassium thiocyanate, the deep red colour, characteristic of ferric thiocyanate, forms at once. The addition of a small amount of sodium formaldehyde sulfoxylate solution to this system containing ferric ion will immediately discharge the colour.

The existence of ferrous ions in this system can be shown by properly testing with alpha-alpha-dipyridyl by known method.

If a dilute hydrogen peroxide solution, which for example may contain 25 cc. of 0.024 M hydrogen peroxide in 500 cc. water, is treated with a dilute solution of sodium formaldehyde sulfoxylate, which may contain 0.001 to 0.005 M, the mutual destruction of the hydrogen peroxide and sodium formaldehyde sulfoxylate is small. This may be shown by following the changes in the system by titrating the sodium formaldehyde sulfoxylate with bromine and subsequently determining the hydrogen peroxide present with ceric sulphate.

Finally, a comparable series of tests will show that a system which contains hydrogen peroxide, sodium formaldehyde sulfoxylate, and small amounts of promoting iron compounds, contains the oxidizing agent, the reducing agent and ferrous ion, and that these three materials can be maintained in the system for a considerable period of time. These results show that, at the existing pH, the sodium formaldehyde sulfoxylate is a suitable reducing agent for practising the invention.

There are two different types of reducing agents which will give satisfactory results in this invention. The first type, which will be described as "active" reducing agents, are such compounds as the sulfoxylate and ascorbic acid, which in themselves rapidly reduce iron compounds. The second group, herein termed "latent" reducing agents are substances which alone are not effective to reduce iron compounds, but which react with hydrogen peroxide to give an active reducing agent. To this class, belong such compounds as glucose, aldehydes, such as butyraldehyde, and ketones, such as acetone. For example, in a system which contains ferric ion, alpha-alpha-dipyridyl, caustic soda, and butyraldehyde, the butyraldehyde does not rapidly reduce the iron. If, however, hydrogen peroxide is added to the system, a pink colour, characteristic of the ferrous iron, alpha-alpha-di-pyridyl complex immediately appears.

Reference to the above Table further indicates that the choice of a metal compound as a promoter will also depend upon the conditions which prevail during the polymerization. The reduced state of the metal compound has been found to be the more active catalyst. Where conditions are such that the reducing agent will not produce and maintain the metal in its reduced state, as for example was found to be the case by tests with a system which

contained copper sulphate and sodium formaldehyde sulfoxylate at a pH between 1 and 5, the system is not one which produces rapid and efficient polymerization.

These systems are particularly useful at temperatures ranging from about 25 to about 60° C., but may be used at higher and lower temperatures if so desired. It has been found generally advantageous to reduce the amount of metal compound promoter which is employed where the polymerization is to be conducted, at higher temperatures.

The amount of reduced heavy metal compound required is generally small. The preferred concentrations, based on the total weight of reactants present generally is from 0.1 to 5 parts per million. Where larger amounts of metal compounds are present, it has usually been found that the consumption of peroxide compound and reducing agent is excessive, although the rate of polymerization is generally increased. Where the system under polymerization is subject to contamination, which introduces excess metal compound over that which is desirable, it has been found possible to add metal complex forming ions to advantage. Thus sodium pyrophosphate, tartrate, or oxalate, can be employed to advantage in systems where contaminating iron compounds are present in such excessive amounts as 15 to 100 parts per million.

The amount of hydrogen peroxide or other oxygen-liberating compounds employed is not unduly critical. It may be varied from 1 or 2 per cent of the weight of the monomer to be polymerized, downwards to several thousandths of a per cent. When the concentration of the peroxygen compound present is too low, the polymerization will be slow and incomplete.

The amount of the reducing agent employed likewise may vary considerably. The quantity used may range from one tenth of the weight of the peroxygen compound to several times that of the peroxygen compound. The most effective method of using these catalyst systems will likewise vary somewhat with the monomer or monomers which are being polymerized. It seems to be generally true that copolymerization of several monomers requires more catalyst than is usually found necessary for the polymerization of the monomers individually. There is, at times, a desired advantage in adding the catalyst to the system in increments, rather than as a single addition at the beginning of the polymerization. This procedure permits a suitable small catalyst concentration to be more nearly continuously maintained.

While we generally prefer to use an iron salt as catalyst activator, the simple (non-complex) soluble compound of other heavy metals capable of existing in more than one state of valence may also be used, for example compounds of titanium, vanadium, cobalt, nickel, copper, cerium, lead and tin.

These activated systems are primarily useful for the so-called emulsion type of polymerization, where the monomer and water are both present, with or without a suitable dispersing agent employed to homogenize the system. As indicated above, it is also possible to employ the process of the invention to advantage, using in place of water, or in addition thereto, other associated hydroxylated liquids having a molecular weight up to 61, such as ethanol or methanol, and in which the metal compounds are more or less ionized.

The process of the present invention is suitable for polymerizing the various polymerizable monoethylenic compounds having the group $\text{CH}_2=\text{C}<$, for example, monomeric mono-vinyl compounds, such as vinyl esters of organic acids, e.g. vinyl acetate, vinyl formate, vinyl butyrate, vinyl benzoate, etc.; vinyl ethers and ketones, e.g., vinyl alkyl ethers and vinyl alkyl ketones; vinyl halides and vinylidene halides, e.g. vinyl chloride and vinylidene chloride; and vinyl aryls, e.g. styrene and substituted styrenes. Also included are acrylic acid and its various derivatives such as methacrylic acid, chloroacrylic acid, and the esters and nitriles of acrylic acid and said derivatives.

This invention is primarily useful for saving time and space. By using the improved process of this invention, it is possible to economically and efficiently polymerize monomers with such inexpensive oxygen-liberating compounds as hydrogen peroxide. Without the use of the activated systems of the present invention, such polymerizations have previously been too slow or incomplete.

We are aware that in British Specification No. 590,191 there is claimed a process which comprises polymerizing an unsaturated organic compound in aqueous emulsion in the presence of a complex cyanide of the group consisting of water-soluble ferricyanides, cobalticyanides, nickelicyanides, molybdicyanides, mercuricyanides, complex cyanides of zinc, copper and silver, mixtures of such complex cyanides, and compounds which are capable of yielding such complex cyanides under the reaction conditions, and we make no claim herein to anything therein claimed.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that, subject to the foregoing disclaimer, what we claim is:—

1. In the process for polymerizing one or more polymerizable mono-ethylenic compounds having the group $\text{CH}_2=\text{C}<$ in the presence of an oxygen-liberating polymerization catalyst and in the presence of water and/or other associated hydroxylated liquid having a molecular weight up to 61, the step which comprises promoting the effect of said catalyst by the presence of a compound of a heavy metal capable of existing in more than one state of valence, said compound being present in a reduced state.

2. In the process of Claim 1 the step of adding also a reducing agent which will maintain at least an effective proportion of the heavy metal compound in the reduced state.

3. In the process of Claim 2 the step of using a reducing agent which is capable of reducing ferric iron compounds to ferrous iron compounds in the presence of the oxygen-liberating compound selected as the polymerization catalyst.

4. In the process of any of the preceding Claims the step of carrying out the polymerization at temperatures ranging from 25 to 60° C.

5. In the process of any of the preceding Claims the step of using an amount of the reduced heavy metal compound of from 0.1 to 5 parts per million based on the total weight of the reactants present.

6. In the process of any of the preceding Claims the step of using, as the reduced heavy metal compound, an iron salt, for example, ferrous sulphate.

7. In the process for polymerizing one or more polymerizable mono-ethylenic compounds having the group $\text{CH}_2=\text{C}<$ in the presence of an oxygen-liberating polymerization catalyst and in the presence of water and/or other associated hydroxylated liquid having a molecular weight up to 61, the step of promoting the effect of said catalyst by the presence of a compound of a heavy metal capable of existing in more than one state of valence, said compound being present in a reduced state, in the manner hereinbefore particularly described and ascertained, especially with reference to the foregoing Examples and Table.

8. Polymers of those mono-ethylenic compounds having the group $\text{CH}_2=\text{C}<$ whenever obtained by a process involving the step or steps of any of the preceding Claims.

607,735

Dated the 9th day of February, 1946.

E. A. BINGEN,
Solicitor for the Applicants.

ND

PUBLISHED BY :-
THE PATENT OFFICE,
25, SOUTHAMPTON BUILDINGS,
LONDON, W.C.2.